

OXIDATION OF 4-ALKYL-HYDROXYIMINO-2,4,6-TRI-t-BUTYL-
2,5-CYCLOHEXADIENES. CONVENIENT METHOD FOR THE
PREPARATION OF 4-ALKYL-2,6-DI-t-BUTYLNITROBENZENES

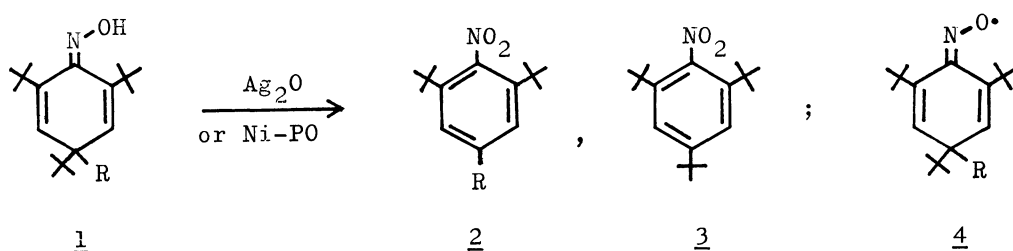
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Reactions of 4-alkyl-1-hydroxyimino-2,4,6-tri-t-butyl-2,5-cyclohexadienes with silver oxide or nickel "peroxide" give 4-alkyl-2,6-di-t-butyl nitrobenzenes, which are otherwise inaccessible without difficulty, in good yields.

In spite of active investigations in the area of poly-t-butylbenzenes,^{1,2)} there is no practical method for the synthesis of 1-substituted 4-alkyl-2,6-di-t-butylbenzenes except for phenols and their derivatives. We now wish to report a convenient synthesis of 4-alkyl-2,6-di-t-butyl nitrobenzenes (2).

The reaction of 4-alkyl-1-hydroxyimino-2,4,6-tri-t-butyl-2,5-cyclohexadienes (1)³⁾ in benzene with excess silver oxide or nickel "peroxide"⁴⁾ at room temperature for 24 hr gave 2 in moderate to excellent yields. The yields for silver oxide oxidation are shown in Table.⁵⁾



a: R=Et; b: R=i-Pr; c: R=CH₂Ph; d: R=1-adamantyl

Oximes	<u>1a</u>	<u>1b</u>	<u>1c</u>	<u>1d</u>
Products	<u>2a</u> (64%)	<u>2b</u> (99%)	<u>2c</u> (68%)	<u>2d</u> (48%) + <u>3</u> (26%)*

* J. Burgers, M.A. Hoefnagel, P.E. Verkade, H. Visser, and R.M. Wepster, Rec. Trav. Chim. Pays-Bas, 77, 491 (1958).

Since the preparation of nitrobenzenes (2) by nitration of the corresponding hydrocarbons is very difficult owing to the two bulky t-butyl groups,⁶⁾ this reaction provides a convenient method for the synthesis of 2. Furthermore, in view of a key role of a nitro-group in synthetic chemistry of aromatic compounds, this

reaction might also give access to other various types of derivatives.¹⁾

Treatment of 1 in benzene with a deficient amount of nickel "peroxide" led to iminoxy radicals (4) as evidenced by their very strong ESR signals.⁷⁾ We consider therefore that 2 is formed via the initially produced iminoxy radical (4). The present reaction is also interesting in that it is a novel type of fragmentation of iminoxy radicals and the first example of the formation of nitro compounds in silver oxide oxidation of oximes.⁸⁾ Further studies on the mechanistic aspect of this reaction and oxidation of 1 with other reagents are currently underway.

References and Notes

- 1) A review: see R. Okazaki, Yuki Gosei Kagaku Kyokaiishi, 32, 704 (1974).
- 2) For more recent examples, see D. Döpp, D. Müller, and K.-H. Sailer, *Tetrahedron Lett.*, 2137 (1974); D. Döpp and H. Weiller, *ibid.*, 2445 (1974); L.R.C. Barclay, D. Griller, and K.U. Ingold, *J. Amer. Chem. Soc.*, 96, 3012 (1974).
- 3) R. Okazaki, Y. Inagaki, and N. Inamoto, *Chem. Commun.*, 1974, 414; *Chem. Lett.*, No. 12 (1974).
- 4) Silver oxide was preferable to nickel "peroxide" for the preparation of 2 because of the clean reaction and the good yield. The oxidation of 1b with nickel "peroxide", for example, led to a complex reaction mixture (7 spots on its TLC) and 2b was obtained in 35% yield.
- 5) The products were purified by preparative thin layer chromatography. All new compounds were characterized by their analytical and spectral (NMR, IR, and MS) data except for 2d where the pure specimen free from 3 has not yet been obtained owing to the similar R_f values of 2d and 3 and the yield was determined by means of high speed liquid chromatography with a UV detector assuming both 2d and 3 have the same molar extinction coefficient at 254 nm. NMR(CCl₄, δ) 2a: 1.22(t, J=8 Hz, 3H), 1.33(s, 18H), 2.62(q, J=8 Hz, 2H), and 7.15(s, 2H); 2b: 1.26(d, J=7 Hz, 6H), 1.37(s, 18H), 2.90(sep, J=7 Hz, 1H), and 7.18(s, 2H); 2c: 1.33(s, 18H), 3.95(s, 2H), and 7.11-7.29(br s, 7H); 2d: 1.37(s, 18H), 1.75-2.40(m, 15H), and 7.32(s, 2H); 3: 1.32(s, 9H), 1.37(s, 18H), and 7.40(s, 2H).
- 6) For instance, nitration of 3,5-di-*t*-butyltoluene affords the corresponding 2- and 4-nitro derivatives in 98.5 and 1.5% yields, respectively. P.C. Mhyre, M. Beug, and L.L. James, *J. Amer. Chem. Soc.*, 90, 2105 (1968).
- 7) For example, the oxidation of 1b gave the spectrum assignable to 4b (triplet of doublets, $g=2.006$, $a_N=33$ G, and $a_H=4$ G). The same spectrum was obtained from 1b with photo-excited benzophenone which has been reported to be an excellent reagent for the formation of an iminoxy radical from an oxime [T.-S. Lin, S.H. Mastin, and N. Ohkaku, *J. Amer. Chem. Soc.*, 95, 6845 (1973)]. When an excess of nickel "peroxide" was used, the triplet of doublets was initially observed, but rapidly changed to a triplet ($g=2.006$, $a_N=32$ G, and no clear coupling due to hydrogens) due to another iminoxy radical. In the oxidation with silver oxide, only the latter type of triplet was observed. These observations as well as the reported formation of an iminoxy radical from an oxime in the oxidation with silver oxide⁸⁾ suggest that 4 is initially formed and converted to the latter type of iminoxy radical for a reason as yet unknown to us. Attempts are now in progress to elucidate the structure of the latter type of iminoxy radical. We thank Prof. K. Tokumaru for helping in ESR measurements.
- 8) J.L. Brokenshire, J.R. Roberts, and K.U. Ingold, *J. Amer. Chem. Soc.*, 94, 7040 (1972); G.D. Mendenhall and K.U. Ingold, *ibid.*, 95, 2963 (1973) and references cited therein.

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